

EXPLOSIVES DETECTION: A Challenge for Physical Chemistry

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ABSTRACT

The detection of explosives, energetic materials, and their associated compounds for security screening, demining, detection of unexploded ordnance, and pollution monitoring is an active area of research. A wide variety of detection methods and an even wider range of physical chemistry issues are involved in this very challenging area. This review focuses on techniques such as optical and mass spectrometry and chromatography for detection of trace amounts of explosives with short response times. We also review techniques for detecting the decomposition fragments of these materials. Molecular data for explosive compounds are reviewed where available.

INTRODUCTION: THE NATURE OF THE THREAT

During the past ten years, the world has been stunned and outraged by a series of assaults on civilian targets that used explosive devices. The destruction of Pan American Flight 103 in 1988 by a bomb secreted in checked baggage, followed by the truck bombings at the World Trade Center in New York City in 1993 and the Murrah Federal Building in Oklahoma City in 1995, as well as an incident at the Centennial Olympic Park (Atlanta, Georgia) in 1996, all led to widespread demands for identification and punishment of the perpetrators, along with calls for improved security measures to prevent such incidents in the future. So sensitized has the public become to the threat of "terrorist bombing"

that when TWA Flight 800 plunged into the ocean near New York City in July 1996, it was widely assumed that a bomb was responsible, even though the FBI found no evidence of a bomb or other terrorist device. In fact, no documented aircraft bombings have occurred since 1989 (1).

The aforementioned events are only the most highly visible of an ongoing series of assaults against a range of targets, including military installations such as the Marine barracks in Beirut, Lebanon, in 1983 and Khobar Towers Barracks in Dhahran, Saudi Arabia, in 1996, as well as numerous civilian targets. During each year of the 1990s, 2000 to 3000 explosives incidents warranting investigation have occurred in the United States, and a comparable number have occurred in other countries including Northern Ireland, Israel, and Russia (2).

In addition to detecting and deactivating targeted explosive devices—or, if necessary, identifying their origin once detonation has occurred—there is an urgent need to locate the 120,000,000 antipersonnel land mines left behind in 62 countries around the world, especially in scenes of recent conflicts such as Bosnia, Croatia, Cambodia, and the Middle East. These abandoned land mines kill or injure 30,000 people each year, 80% of them civilians (3, 4). It is not only deliberately emplaced explosives that are of concern: Large amounts of unexploded ordnance and explosive residues contaminate former military installations, often preventing the decommissioning of such sites and their return to civilian use. It was remarked at the 1995 Bureau of Alcohol, Tobacco, and Firearms (BATF) Symposium on the Analysis and Detection of Explosives (4a) that “. . . security, forensic, and environmental demands for identification, detection, and removal of explosive materials are converging on a common set of requirements.” Similar capabilities are required for detection of illegal drugs and other contraband materials (5).

In response to these challenges, major efforts have been undertaken in the United States and other countries to develop, certify, and deploy explosives detection systems (6–16). In accordance with the often expressed view that “the most effective measures for preventing acts of terror are usually technological” (17), many of these systems rely on elaborate, state-of-the-art instrumentation to detect explosive materials before they can reach their intended target. These detection systems are of two basic types. *Bulk detection systems* rely on X-ray or neutron imaging to locate large quantities of explosive materials. Several such systems, widely employed in airport security applications, have been described previously (6–10, 15). We focus on *vapor and particle detection systems*, with which trace quantities of explosives are detected via a molecular signature. Such trace detection systems could avoid some of the difficulties associated with the bulk systems (1, 7). While most detection techniques are designed for high-explosive materials such as trinitrotoluene (TNT), cyclonite

(hexahydro-1,3,5-trinitro-1,3,5-triazine, RDX), and pentaerythritol tetranitrate (PETN) (see Table 1), a wide variety of other explosive materials, such as ANFO (ammonium nitrate/fuel oil mixtures), has been encountered in bombing incidents (18). Because volatile molecular species such as ethylene glycol dinitrate (EGDN), dimethyldinitrobutane, mononitrobenzene, or isotopically labeled explosives have been endorsed for "tagging" commercial explosives as a means of source identification, we consider these substances as well (19).

Detection of explosives at the molecular level can potentially employ a wide variety of analytical techniques. In order to assess the feasibility of such techniques and design viable detection systems, molecular properties and spectroscopic signatures of the target molecules are needed. We review these, along with a survey of techniques and methods currently under development. The focus of this review is material published or presented in open conferences between 1992 and 1997. Earlier sources and references to other detection techniques and to systems and policy aspects of this complex problem may be found in the cited reviews, monographs, and conference proceedings (6–15, 18, 20, 21).

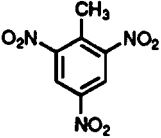
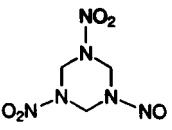
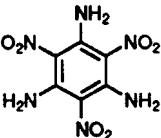
PHYSICAL CONSTRAINTS ON EXPLOSIVES DETECTION

Vapor Pressures

Vapor detection methods must contend with the fact that room temperature vapor pressures of many common explosives are small, and the vapor pressures of some of the materials with the highest priority for detection are especially so. Table 1 lists several properties of a set of selected explosives. Additional properties of these substances, along with those of many other explosive materials, are given in the review by Oxley (18). The dramatic increase in vapor pressures between room temperature and an elevated temperature (400 K, in this example) is the basis for several sampling techniques.

Some common explosives are actually solid solutions of ingredients such as those in Table 1; thus, the vapor pressures of these mixtures can be substantially depressed compared with those of the pure components. For example, McGann et al (26) showed that the detection of the RDX-containing explosive C-4 would require two orders of magnitude higher sensitivity to vapor than required for detection of RDX itself. Both entries in Table 1 for the common impurity and additive EGDN have substantial uncertainty at room temperature because of solution effects and at elevated temperatures because vapor concentrations may remain below an explosion limit (extrapolation of the vapor pressure expression, based on measurements to 300 K, would yield an EGDN vapor pressure of

Table 1 Properties of selected explosives and related materials

Acronym	Name	Formula	Equilibrium vapor pressure ^a (ppb _v)	
			300 K	400 K
EGDN	Ethylene glycol dinitrate	CH_2ONO_2 CH_2ONO_2	1.2×10^{5b}	Explodes at 387 K
NG	Nitroglycerine	CH_2ONO_2 HCONO_2 CH_2ONO_2	740	5.1×10^6
TNT	Trinitrotoluene		13	4.7×10^5
RDX	Cyclonite, hexahydro-1,3,5-trinitro-1,3,5-triazine		0.0084 ^c	2.1×10^3
PETN	Pentaerythritol tetranitrate	CH_2ONO_2 $\text{O}_2\text{NOCH}_2\text{-C-CH}_2\text{ONO}_2$ CH_2ONO_2	0.026	2.8×10^4
TATB	1,3,5-Triamino-2,4,6-trinitrobenzene		3.6×10^{-9d}	7.6×10^{-2}
AN	Ammonium nitrate	NH_4NO_3	e	
UN	Urea nitrate	$\text{NH}_2\text{C}(\text{NH}_2)\text{NO}_3^-$ O		

^aVapor pressures from Reference 22 unless otherwise noted.^bFrom Reference 23.^cExperiments with PCP and Varian vapor generators suggest that the vapor pressure of RDX may be six to eight times higher than that indicated in the Dionne article (Reference 22), e.g. 8.2 ppb, at $T = 333$ K (RM Stimac, unpublished measurements).^dFrom Reference 24.^eThe vapor pressure of ammonium nitrate reported by Dionne et al (22) is similar to that of TNT over this temperature range. However, on the basis of our infrared measurements (70) and theoretical calculations of the binding energy (25), it appears that AN evaporates and condenses as dissociated components (ammonia, nitric acid vapor) rather than as molecular ammonium nitrate.

9.5×10^7 ppb_v at 400 K). The International Civil Aviation Authority (ICAO) has specified EGDN as one of four taggants intended to enhance the detectability of explosives (27), so EGDN's high vapor pressure is of interest not only for calculations of detection sensitivity, but also for estimation of the useful lifetime of tagging.

Limited Sample Size

A key issue in explosives detection is the orders of magnitude difference between the density of solid explosives and the density of even saturated explosives vapor. Detectable amounts of explosives can be obtained in microscopic solid-phase samples, whereas accumulation of a detectable amount from vapor sampling may require the sampling of a large volume of air, coupled with various techniques to raise vapor pressures and aid vapor transport. Griffy's (28) calculations for current vapor sampling scenarios show dilution by many orders of magnitude from equilibrium vapor levels. Fine & Achter (29) remarked that total sample weights derived from high-volume air sampling for vapor could well be in the 0.01–0.001 pg range. By comparison (from several studies reviewed in the section on Calibration Techniques/Protocols, below) a single first-generation C-4 fingerprint can yield several micrograms of RDX.

Deliberate Concealment

Another factor that could make vapor sampling an even greater challenge than particle sampling is the fact that individuals making and placing bombs attempt to conceal their handiwork. If even one particle can be collected by a screening system, it may be detected. On the other hand, while even the most fastidious clean-up might leave behind one solid particle, in principle it should be possible to seal up the bulk explosive so that no vapor can escape. The total weights from vapor sampling quoted above do not take into account any attempts at wrapping the explosive. Davidson et al (30) summarize a section on attenuation of vapors by saying that in their experience, "only the most volatile species can be detected under 'real-world' conditions" because of the attenuation of vapors by packaging materials and adsorption of the vapors on the materials within the container. Kolla (8) suggests that a rough order of magnitude estimate of the effect of wrapping is a decrease in vapor concentrations by a factor of 1000.

Interferences

Characterizing the response of a given detection method to the explosives it is designed to detect is a difficult enough task, and yet in some sense we eventually need to know the responses of the method to all other substances as well before confidence in it can be established. All techniques have interference problems, and in a few cases, field trials extensive enough to generate false

alarm statistics have been carried out. For example, in October 1988, the Thermedics Detection EGIS thermal decomposition/gas chromatography/NO chemiluminescence detection system was deployed at Boston's Logan Airport and performed tests on over 2000 volunteers, with a false positive rate of less than 0.15% (no discussion of possible sources of false positives was given) (31).

In their discussion of false alarm rates for the British Aerospace CONDOR tandem mass spectrometric instrument, Davidson et al (30) distinguish between "nuisance" alarms involving detection of trace amounts of the target compound in which no bulk compound is present and "actual" false alarms involving response to compounds other than the target compounds. They reported false alarm rates for a study of over 20,000 cargo containers and vehicles, with the strong implication that their tandem mass spectroscopy (MS/MS) technique was selective enough that very few actual false alarms were involved. For example, a TNT detection threshold of 50 pg led to a false alarm rate of 0.13%. They also discussed the use of signature compounds, which are not explosives themselves but which are otherwise associated with explosive formulations, such as solvents, additives, or impurities. In one example, using the additive and impurity EGDN as a signature compound for dynamite led to a false alarm rate of less than 1%, with no common compounds identified as interferences. However, the use of the solvent cyclohexanone to detect C-4 led to a false alarm rate of over 20% as a result of interferences from solvents, rubber products, and some plastics, leading to its abandonment as a signature compound.

A comparison of two reviews illustrates the difficulty of reducing such anecdotal evidence to summary statements covering whole techniques. In 1995, Kolla (32) reviewed the vapor detection techniques of MS, ion mobility spectrometry (IMS), and gas chromatography with electron capture detection (GC/ECD) and with chemiluminescence detection (GC/CD). Kolla essentially dismissed MS because of its lack of selectivity, called GC/ECD the least reliable technique because of its selectivity problems, and said that IMS and GC/CD had advantages over the other techniques in selectivity, even though in each case false positives were still possible. On the other hand, in 1992, Nyden (20) rated GC/ECD and MS/MS as "excellent" in selectivity but rated IMS and GC/CD as only "good." Part of this difference stems from which basic technique is implemented—MS and MS/MS are indeed poles apart in selectivity. Between the broad array of techniques and the even longer list of possible interfering compounds, it is clear why the area of interferences still needs attention.

Sampling and Surface Contamination Phenomenology

Several recent papers provide useful reviews of sampling options (29, 33–35). A common observation, already noted above, is that vapor sampling will result

in very small samples for some key explosives, while particle sampling may yield much more easily detectable samples.

COLLECTORS, PRECONCENTRATORS, AND HAND-HELD SAMPLERS We make a fairly artificial distinction between sampling techniques developed for portal screening (and therefore eventually interfacing with a detector in a fixed installation) and those developed for hand-held applications (although the sampling device is hand-held, the detector may be either integrated into it or fixed). A variety of collection techniques for portal screening have been described. These include vapor suction or particle removal by wiping or vacuuming; collection on metal screens, tubes, plates, or Teflon filters; and thermal desorption by activating a heater in the collection device or insertion of the collecting surface into a heater (34, 36–38). A particularly detailed discussion of the collector, a spiral ribbon metal surface collector/concentrator, used in the Thermedics Detection EGIS GC/CD device has been given (39). Several groups have developed devices—such as a rotary preconcentrator (26, 40), a rotating disk trap rotating between the impinging sampled air flow and a thermal desorption region, a rotating wheel of Teflon membrane filters operating in a similar manner (41), and a mesh belt transporting samples between collection and desorption regions (37)—that turn these batch sampling techniques into continuous sampling. The use of membrane preconcentrators is being actively studied (42, 43), and useful overall discussions of sampling issues are available (29, 30, 34).

Sheldon et al (35) provide a comprehensive discussion of sampling alternatives, focusing on hand-held applications. Among the options are direct desorption, vacuum collection of particles, and wiping followed by vacuuming. Bromberg et al (44) provide a detailed discussion of the first option, in which a projection lamp is used to heat the substrates being sampled.

PORTALS Portals are devices designed to extract samples (potentially including explosive vapors or particles, for instance) from people. An important issue is how to do this without treating passengers as if they were baggage. Portals that rely on noncontact sampling have used high-velocity airflows to break up vapor-rich boundary layers. However, as seen in Griffy's (28) calculations, although vapor diffusion is so slow that concentrations outside the boundary layer remain much lower than equilibrium, efforts to transport vapor out of the boundary layer using large air flows result in dilution. He concludes that concentrations in sampled air will be many orders of magnitude lower than equilibrium levels. On the other hand, Settles et al (45) point out that the natural convection induced by the heat of the human body leads to vapor transport at low flow rates (and hence higher concentrations), so if this human thermal plume could be captured

without dilution, vapor sampling could yield explosives amounts detectable by existing methods.

At least two groups have designed and tested portals using air jets to dislodge vapor and particles from passengers without physically contacting them (29, 31, 46). Hobbs & Conde (47) and Achter et al (31) presented airflow calculations for two designs for noncontact passenger screening booths. Hobbs & Conde presented absolute concentrations, under steady-state conditions, in units of grams of RDX per mole of air.

Portals that are intended to carry out contact sampling rely on the passenger to create the contact, as in the intimate sampling walk-through portal (26) in which several sets of paddles containing air inlets are pushed aside like frontier saloon doors. This portal system (with an IMS detector) reportedly responds to subpicogram quantities of RDX in 6 s. The portal design reported by Wendel et al (41), although the direct descendant of the noncontact portal described by Achter et al (31) that used air jets and infrared (IR) heaters to enhance evaporation and stimulate particle entrainment, uses a similar set of sampling wands in the form of paddles, each with many inlet holes for vacuum sampling.

SURFACE CONTAMINATION The explosive is not the only material whose properties must be considered for a full understanding of either vapor or particle sampling. For example, Bender et al (48) showed that TNT vapor adsorbed to and desorbed from surfaces over periods of days. Their interest was to show that contaminated surfaces serve as sources of TNT vapor, leading to increased chances of detection. However, Davidson et al (30) pointed out another side of vapor transport, in which vapor pressures remain far below equilibrium levels, while surfaces act as sinks. An example of work in the particle area is the study by Liu et al (49) quantifying the adhesion forces between particles and substrates by measuring particle detachment velocities. Compositions of both particles and surfaces were varied, along with particle diameters and the techniques of deposition, although only a few studies were reported of explosive particles. It is clear that more investigations could be made into the basic physical chemistry parameters involved in vapor transport, particle contamination, and sampling and concentration techniques: Measurements of diffusion coefficients, molecular sticking coefficients, vapor pressures over nonideal solutions, partitioning in solvents, particle adhesion forces, and particle morphologies for the materials of interest are all scarce.

CALIBRATION TECHNIQUES/TESTING PROTOCOLS Many of the detection techniques under consideration involve processes that require calibration, and as a result, an extensive literature on calibration techniques has appeared. The

current application of these techniques is the initial determination of the sensitivity of detection methods as they undergo development. Many of these studies contain useful information about the phenomenology of explosives detection because they are to some extent simulations of real explosives detection scenarios. Both vapor and solid (particle) generators are discussed here.

Vapor Generators Several groups (50, 51) have evaluated the use of the collector or preconcentrator of their sampling system as a calibrated pulsed source of explosives vapor. In this application, known solid particle weights or dried solution volumes can be deposited and then thermally desorbed into the detection device. A number of other sources involving thermal desorption of solid explosives into a gas flow have been reported (22, 52, 53). Macdonald & Rounbehler (54) simply used a solution-soaked piece of paper as a vapor source, while Lucero et al (55) designed a system based on a permeation bag to deliver very low concentration levels.

Solid Phase Generators Davies et al (56) described a development program that applied two sophisticated particle generation techniques: a vibrating orifice aerosol generator (involving evaporation of monodisperse liquid solution droplets) and a fluidized bed generator (which uses dry powder as the feed material). This program responded to a need for better-controlled standard particle sources than those evaluated to that point. Considering the range of goals that might be set for a calibration technique, from quick assessments of a fielded device to quantitative simulation to better understand basic mechanisms, it is not surprising that techniques considered should range from simple to sophisticated. For example, Macdonald & Rounbehler (54) dipped wooden craft sticks in explosives solutions as their calibration technique, followed by solvent evaporation and subsequent vacuuming.

The simulated fingerprint (57) is a particularly important technique, though recognized to involve many variables that are difficult to control quantitatively. The use of calibrated thumbprints has been studied by at least two groups (58, 59). Depending on one's point of view, the following can be taken as documenting either a larger level of variability than is ideal in a calibration method or a remarkable level of reproducibility in a realistic simulation of a "real-world" process. Of particular interest are the high levels of explosive deposited in the first fingerprints after contact with the explosive and the persistence of measurable explosive after repeated prints: The two groups' (58, 59) RDX weights in a first thumbprint after handling Semtex (collected by acetone washing) are about 4.5 and 3 mg, with the tenth print still containing around 100 ng (58) and the fiftieth print averaging 14 ng (with lower and upper bounds of 3 and 76 ng). Results of particle size analysis have also been presented (59), showing in the

first few prints a distribution with two modes in the 30–150 and 150–350 μm ranges. We can note that a 150- μm -diameter solid particle has $1.8 \times 10^{-6} \text{ cm}^3$ volume and thus contains about 2 μg of RDX.

Strategies for Overcoming Constraints

Recently, several options for increasing detection sensitivity have become available, including sample treatment techniques such as preconcentration or separation, data analysis techniques such as spectral pattern recognition, and other chemometric techniques for maximizing signal-to-noise (S/N) ratios. Although these techniques have been widely employed elsewhere and are currently under study in explosives detection contexts, we are not yet in a position to quote published studies in which improvements in detection limits are quantified by comparison to less sophisticated techniques. Furthermore, a common opinion in the community is that detection techniques with adequate sensitivity and selectivity exist and that the greatest progress is required in areas involving sampling from passengers, luggage, vehicles, and other sources.

SPECTROSCOPIC TECHNIQUES FOR EXPLOSIVES DETECTION

Optical spectroscopy, while widely used for measurement of many different species at trace levels or in complex backgrounds, has not been extensively applied to explosives detection. This is due in part to the physical constraints noted above—low vapor pressure, limited sample size, concealment, interferences—and in part to the spectral characteristics of the compounds themselves. At the present time, however, there is considerable interest in and active investigation of spectroscopic techniques as the basis for possible detection systems. For any such detection scheme, the essential information required is data on wavelengths and intensities corresponding to absorption and/or emission features of the target compounds. While such data are not yet available in a form as systematic as, say, the Sadtler Index for organic compounds or the HITRAN database for atmospheric absorbers (60), a considerable amount of data on the spectroscopy of explosive compounds is available in the literature and is reviewed in this section.

Infrared Spectroscopy

Condensed-phase mid-IR spectra of TNT, RDX, PETN, and a wide range of other explosives, boosters, primers, propellants, incendiaries, and related materials have been available for many years (61–63). Near-IR spectra of several of these species have also been measured between 1.0 and 2.3 μm using a scanning acousto-optic tunable filter spectrometer (64, 65). The materials studied all show

a prominent absorption between 1.5 and 1.7 μm , but these bands may be associated with an overtone of a C-H stretching vibration (or N-H, in the case of ammonium salts), rather than with the more characteristic NO_2 vibrational modes (66).

Spectral data for these materials in the vapor phase are more limited. Acousto-optic measurements of absorption by EGDN, nitroglycerine, and dinitrotoluene vapors in the 6 μm and 11 μm regions have been reported (67), but data are more limited for less volatile species (see Table 1). In a set of measurements on RDX in solid, solution, and vapor phases (68), the vapor was obtained by flash desorption of RDX from a nichrome filament, making absolute intensity measurements impossible and resulting in interference by decomposition products. IR spectra of TNT and several ^2H - and ^{15}N -substituted isotopomers have been recorded and compared with calculations at the MNDO level (69). Janni et al (70) have obtained vapor absorption spectra for TNT, RDX, and PETN in heated static cells and have reported absolute band intensities for these systems. A similar measurement on ammonium nitrate revealed only absorptions due to dissociated ammonia and nitric acid vapors (and a decomposition product, N_2O), as expected on the basis of earlier measurements (71, 72) and recent calculations (25) for this system. These IR measurements are summarized for convenience in Table 2.

Also listed in Table 2 are several examples of the use of IR spectroscopy in detection schemes. In a typical example, Hong et al (73) used IR spectrometry, along with GC/MS and spot tests, to identify RDX and diazodinitrophenol in residues obtained from explosive devices smuggled into Taiwan. Fourier transform IR spectroscopy has been used to detect TNT and the more volatile dinitrotoluene desorbed from soil samples (75); several hundred micrograms of each species were detected. A further important application of IR spectrometry to these systems is the use of techniques such as diffuse reflectance IR-FT (DRIFT) or attenuated total reflectance to measure adsorption, decomposition, and diffusion kinetics of species such as EGDN and TNT (79–81).

The difficulty associated with using IR spectrometry as a vapor detection technique lies in the small amount of sample available in most detection scenarios (typically nanograms to picograms), which leads to extremely low net absorbances. Attempts have been made to address this problem by using an indirect means of detecting absorbed IR energy, such as photoacoustic spectroscopy (67, 74) or laser interferometric calorimetry (82, 83), but with limited success. Newer high-sensitivity laser-based methods, such as cavity ringdown spectroscopy, may be able to address this problem more effectively, as we describe in the Conclusions section. A somewhat different approach involves the decomposition of the explosive material to more easily detectable molecular fragments (such as nitrogen oxides) and detection of the fragments; we discuss this in more detail below.

Table 2 Infrared spectroscopic data for explosives and related molecules

Technique	Species	Information or data	References
IR (absorption, reflectance)	NM, GAP, TAGN, TNT, RDX, PETN, AN, NH ₄ ClO ₄	Near-IR spectra (1.0–1.8 μm)	64
IR	HMX, RDX, PETN, TAGN, NM	Near-IR spectra (1.2–2.3 μm)	65
IR	RDX, compositions	Identification	73
IR optoacoustic	EGDN, interferents	CO ₂ laser wavelengths	74
IR optoacoustic	EGDN, NG, TNT	CO and CO ₂ laser wavelengths	67
IR (vapor absorption)	TNT	² H, ¹⁵ N isotopic substitutions	69
IR (vapor absorption)	TNT, RDX, PETN, "AN"	Vapor absorption cross sections	70
IR	RDX (solid)	IR spectrum	63
IR	RDX (solid, solution, "vapor")	Decomposition product in vapor	68
IR	68 materials (condensed phase)	Low-resolution 2–15 μm	61
IR	50 additional materials	Low-resolution 2.5–50 μm	62
IR	DNT, TNT	FTIR/desorption from soil	75
IR (FMS)	RDX	Detect as N ₂ O fragments	76, 77
IR (TILDAS)	TNT	Detect as NO, NO ₂ fragments	78

Raman Spectroscopy

Raman spectroscopy (inelastic light scattering) complements IR spectroscopy as a method for obtaining vibrational information about molecular species. In Raman spectroscopy, this information is transferred from the IR to the visible or near-IR part of the spectrum, where brighter sources and more efficient detectors are available. While Raman spectra are available for most explosive materials of interest (Table 3), it is only recently that this method has emerged as a promising tool for trace level detection. The two principal limitations associated with Raman spectroscopy are the intrinsic weakness of the Raman scattering process itself and the cumbersome instrumentation that until recently

Table 3 Raman spectroscopic data for explosives and related molecules

Technique	Species	Information or data	References
Raman	RDX	632.8 nm excitation	63
Raman	NG, PETN, RDX, TNT	20–40 ng detected on activated charcoal	84
FT-Raman	RDX, PETN,	Component identification Semtex	85
FT-Raman	32 materials	10 μm sample size	86
FT-Raman	RDX	Vibrational frequencies used to estimate impact sensitivity	87
Raman microscopy	RDX, PETN	1 (μm) ³ sample size	88
Raman	PETN	Fiber-optic probe	89
FT-Raman	HMX, RDX, PETN, nitroguanidine, nitrocellulose		90
FT-Raman	HMX, RDX, PETN, nitroguanidine, nitrocellulose	Low-frequency modes	91
SERS	TNT	1 pg TNT detected	92
Raman microprobe	RDX		93
Raman imaging	RDX, PETN		94
Single-pulse Raman	TNB, MATB, DATB, TATB		95–97

was required for Raman spectroscopy. The latter problem has been overcome by advances in Raman instrumentation, such as Fourier transform Raman (98), and especially the recent development of compact diode-laser-pumped CCD-based Raman spectrometers, which are now finding increasing use as analytical measurement and process control tools. These instruments can be used in a confocal imaging or scanning mode to acquire Raman spectra of small solid particles, which makes this technique a very promising approach for detecting explosive residues in post-blast debris, forensic samples such as fingerprints or clothing smears, and (if suitable sampling protocols are employed) possibly for security screening of airline baggage (88, 93, 94). Raman spectroscopy is also a useful tool for probing the dynamics of energetic materials: Trott and coworkers (95–97) used single-pulse Raman to study the behavior of TATB under high pressure, and McNesby & Coffey (87) used Raman data on RDX to estimate the compound's impact sensitivity.

The low sensitivity of Raman spectroscopy can, in principle, be overcome by either of two enhancement methods: resonance enhancement (RRS) or surface enhancement. Resonance enhancement occurs when the Raman excitation wavelength is close to an allowed optical transition of the molecular species (99, 100). The source of the enhancement can be seen from the expression below for the Raman scattering cross section,

$$\alpha_{\rho\sigma} = \frac{1}{\hbar} \sum_e \left(\frac{\langle f | \mu_\rho | e \rangle \langle e | \mu_\sigma | g \rangle}{\nu_{eg} - \nu_0 + i\Gamma_e} + \frac{\langle f | \mu_\sigma | e \rangle \langle e | \mu_\rho | g \rangle}{\nu_{ef} + \nu_0 + i\Gamma_e} \right). \quad 1.$$

The Raman scattering cross section arises from matrix elements of the polarizability tensor between initial, intermediate, and final molecular states. In Equation 1, μ is a transition dipole moment operator, ρ and σ are polarization directions, g , e , and f represent ground, excited intermediate, and final molecular states, respectively, and Γ_e is the width of excited state $|e\rangle$, which acts as a damping factor. In normal or nonresonant Raman spectroscopy, the optical frequency ν_0 is not close to any fundamental transition frequency between electronic states. In RRS, the excitation frequency is tuned to near-coincidence with an electronic absorption feature, driving the frequency difference $\nu_{eg} - \nu_0$ in the resonance denominator of the first term of Equation 1 to nearly zero. This can result in an enhancement of the Raman cross section (α) $_{\rho\sigma}$ by a factor of 10^3 to 10^4 .

The dependence on transition moment in Equation 1 determines which bands and combination of bands will be enhanced. For nitroaromatics such as TNT, the $\pi - \pi^*$ electronic transition is formally forbidden, so the electronic transition moment is zero. A nonzero transition moment, and thus absorption intensity, results from vibronic coupling with nontotally symmetric modes of the electronically excited state. As a result of such coupling, the UV resonance Raman intensities show marked variation with ν_0 as the excitation frequency is scanned across the vibronic components of the absorption band (101).

Surface-enhanced Raman scattering (SERS), initially discovered by Fleischmann et al in 1974 (102), occurs when the Raman-active molecule is adsorbed on a rough metallic surface (103). Largely as a result of a local field enhancement in the metallic particles at which the analyte is adsorbed, up to six orders of magnitude enhancement in the effective Raman scattering cross section can be obtained. Indeed, a favorable combination of resonance and surface enhancement has made it possible to detect single dye molecules using Raman spectroscopy (104). Using colloidal gold solution as the SERS-active medium and near-IR (830 nm) excitation, TNT has been detected at 7.5×10^{-7} M concentration, corresponding to ca 1 pg of TNT in the sampled volume (92).

The primary difficulty with SERS is its lack of reproducibility, which results from the variable properties of the metallic surface (or colloid) at which the analyte is adsorbed. In an attempt to obtain both sensitive and reproducible

detection, self-assembled monolayers incorporating colloidal metal particles are being investigated as SERS substrates (105, 106). Initial results with these substrates show sensitivity comparable to that obtained with the colloidal metal sols (106a).

UV/Visible Spectroscopy

The broad and featureless electronic absorption spectra of nitroaromatic and nitroaliphatic molecules are found, for the most part, at wavelengths below 300 nm. This is the region in which most organic molecules possess strong absorption bands, making selective detection of explosive compounds via UV absorption difficult or impossible. Additional very weak absorptions between 400 and 1600 nm have been recorded for TNT, RDX, PETN, and other energetic materials using photoacoustic spectroscopy (107), but these absorptions are also not suitable for detection purposes. The limited spectral data in this region are summarized in Table 4.

These spectra are valuable, however, for optimizing other measurement schemes employing more sensitive and specific detection techniques. The resonance Raman method, for example, requires an excitation wavelength coinciding with an allowed optical absorption. The spectra obtained by Mercado et al (101) indicate that the optimum wavelengths for UVRRS in TNT lie between 200 and 300 nm, while RDX and especially PETN require wavelengths at the lower end of this range, which are more difficult to generate. An allowed electronic transition is also the first step in resonant multiphoton ionization (REMPI), which when combined with time-of-flight (TOF) mass spectrometry,

Table 4 UV/Visible spectroscopic data for explosives and related molecules

Technique	Species	Information or data	References
Spectrophotometry	TNT, RDX, PETN	Absorption spectra 200–400 nm	101
Photoacoustic spectroscopy	RDX, HMX, PETN, TNT, 14 others	400–1600 nm	107
Chemiluminescence	RDX, PETN	During thermal decomposition	108
Optical	Nitrocellulose deflagration	Detect burning rate	109
Fragment	TNT fluorescence	Detect NO fragment at 226 nm	110
IRMPD + fragment	RDX, HMX fluorescence	Detect OH fragment	111

can provide highly sensitive and specific detection. This is discussed further below.

Hargis (112) has reported detection of ANFO mixtures by UV fluorescence. The explosive may be discriminated from background materials by multispectral analysis, and this method possesses stand-off remote sensing capability. UV-excited emission from other explosive materials is also being measured (112a). UV and visible emissions from fragments and decomposition products have been observed, as described in the following section.

FRAGMENTATION AND FRAGMENT DETECTION

Unlike the other techniques discussed in this review, the investigations described in this section are united not by a particular instrument but by a common approach. Through thermal or laser decomposition techniques, explosive molecules are made to yield small gaseous molecules, which can then be detected. In most of the cases reviewed here, the decomposition product molecule is NO, which can be detected by a variety of highly sensitive techniques.

This class of techniques includes one of the instruments most extensively deployed in airport screening applications, the Thermedics Detection EGIS system (34, 113). Thermal decomposition occurs as part of the step of thermal desorption from the collector of the sampling system, a spiral of metal ribbon. The products of the desorption step pass through a sequential pair of high-speed gas chromatographs to a chemiluminescent nitric-oxide-specific detector. While not reported in detail, detection limits for common explosives appear to be less than 1 pg (113). A laboratory and field evaluation (114) showed good behavior against many possible interferences. A low level of false alarms is expected as a result of several selectivity mechanisms involved in the system [by one count, each sample is subjected to 18 yes-or-no questions, or “dichotomous keys” (115)].

The thermal decomposition/frequency-modulated IR diode laser system, which has been investigated by Riris et al (76), seeks to detect decomposition products in addition to NO. Riris et al (76) reported a 5–10 pg detection limit for RDX, based on observations of N₂O. The system should also have been capable of measuring NO fragments, but none were detected. Mercado & Davies (77) performed an evaluation of this instrument using absorption by NO at a single IR wavelength and estimated a detection limit for RDX of 50 pg at S/N = 4. Detection of PETN was attempted but was hampered by interference from water. Researchers continue to improve both the capabilities and the ease of use of tunable diode laser systems, including detection of N₂O, NO, and NO₂ in studies of atmospheric trace gases (116, 117), combustion exhausts (117, 118), and explosives decomposition systems (119). However, the

expense and complexity of these systems means that their most likely contribution to explosives screening will be in the development of other IR techniques.

A variety of fragments were detected following thermal decomposition of RDX using Stark-modulated millimeter-wave spectroscopy and Fabry-Perot cavity Fourier transform microwave spectroscopy (120). Species detected included HCN, CO, H₂CO, NO, N₂O, NO₂, HNCO, HONO, NH₂CHO, and HCOOH. The emphasis in this work was on identification of decomposition pathways, rather than high-sensitivity detection of the explosive molecule itself.

Another device based on thermal decomposition and fragment detection lies at the other extreme of size, expense, and complexity from tunable diode laser or millimeter-wave absorption: the Scintrex EVD-3000. Nacson et al (38) reported on this device, which detects NO by use of an electrochemical sensor. They reported a detection limit for PETN of less than 50 ng with an 8-s analysis time. Although deficiencies in both the sensitivity and selectivity of this device prevent its use in some screening applications, its small size and weight and fast response time offer strong advantages in other applications.

Several groups have investigated laser decomposition techniques. In particular, laser decomposition of explosives vapors and subsequent multiphoton ionization of the NO product can be accomplished using the same laser wavelength. Lemire et al (121) reported on an excimer laser-pumped dye laser system coupled to a TOF mass spectrometer that yielded detection limits of 3 pg for TNT and 1 pg for RDX (or, under their sampling conditions, 24 ppb_v and 88 ppb_v vapor concentrations, respectively). Seeking to simplify to a single laser, these workers (122) also investigated an ArF laser system that gave a 210 ppb_v limit of detection for TNT. Several researchers (123–134) have used a doubled XeCl excimer laser-pumped dye laser operating in the 224–230 nm wavelength range to fragment nitroaromatic vapors and ionize the resulting NO, again followed by TOF mass spectrometric detection. This technique has given femtogram limits of detection (123), although these researchers (123–134) refer to laser desorption ionization (of solid or particulate samples) followed by TOF mass spectrometry as having typical sensitivities of 10–100 pg.

Several variants of optical spectroscopy have been proposed for detection of combustion or fragmentation products of explosive vapors and particles. Crowson et al (108) observed visible luminescence from nitroorganic vapors, including RDX and PETN, undergoing thermal decomposition in a tube furnace. Funsten & McComas (109) reported an “optical deflagration” signature for nitrocellulose, which is the time profile of the visible emission from particles of the substance when they are flash-heated. They claimed that the emission from explosive materials shows much faster rise and decay times than from other combustible materials and that this could serve as the basis for selective detection of explosives.

We note here that the current technique of detecting soil contamination by energetic materials also relies on fragmentation (78, 135, 136). A cone penetrometer probe is driven into the ground with a heated section that carries out the thermal decomposition. The gaseous products are drawn into the probe and detected by electrochemical cells. Laser detection techniques for soil contamination are currently under investigation. For example, TNT has been detected by laser photofragmentation of the vapor followed by NO laser-induced fluorescence excited by the same 226-nm light (110).

MASS AND ION MOBILITY SPECTROMETRIES AND CHROMATOGRAPHY

Mass Spectrometric Detection

Mass spectrometric systems have long had to contend with the reputation of being large devices suitable only for laboratory use. Significant miniaturization is now possible, and sensitivity and selectivity levels have been achieved such that, as McLuckey et al (137) said of their atmospheric-sampling glow discharge ionization (ASGDI), quadrupole ion trap mass spectrometer (ITMS, discussed further below), "there are no major technical barriers to its use in the field for trace detection scenarios, provided effective sampling and introduction procedures for the specific application are employed." In 1993, Jankowski et al (33) were trying to integrate a triple quadrupole mass spectrometer system with a vapor portal. In his 1991 review, Yinon (138) cited the SCIEX/British Aerospace CONDOR system, which uses an atmospheric pressure ionization (API) source in negative ion mode with ambient air as the reagent, as well as two systems investigated by the McLuckey group: a quadrupole/TOF MS/MS system, said to have a 3 ppt_v detection limit (explosive compound not specified) or 10 times greater sensitivity with preconcentration, and an ITMS MS/MS system that obtained a CID (collision-induced dissociation) spectrum from 0.5 pg TNT.

In the remainder of this section we review subsequent developments in the area of mass spectrometric detection. We focus on reported detection limits, even though this slight important work on technique development in which detection limits were not evaluated. For that matter, workers who did present such limits were often pursuing goals other than optimization of device sensitivity. However, we wish to convey the point that the sensitivity of mass spectrometry is already adequate to the demands of many screening tasks, and we feel the importance of this point justifies our focus.

Those workers reviewed here who do not report sensitivity levels, as well as several who do, are concerned with improving selectivity, an issue still cited by Kolla in his 1997 review (8) as a potential drawback of mass spectrometry. The

use of MS/MS systems, already noted above, is one well-known and powerful technique (139). Many other groups have studied various ionization techniques, seeking to simplify fragmentation patterns and preserve molecular (or pseudo-molecular) ions [see Yinon (140) for a review of the problems encountered using electron impact ionization as well as several other techniques]. These investigations include low-pressure methane chemical ionization (CI) applied to nitramines (141); direct-exposure probe mass spectrometry applied to RDX and HMX (142); reverse electron attachment detection (READ) applied to RDX, PETN, and TNT (143–146); chloride ion reagent addition in API applied to HMX and more (147) and to RDX and PETN (148); ion cyclotron resonance (ICR) ion molecule reactions with NO^+ as reagent, applied to nitrotoluenes (149); self-chemical ionization, electron capture (EC), and laser desorption ionization (LDI) applied to RDX, PETN, and more (150, 151); studies of negative-ion formation from TNT (152); and chemical ionization using trimethylsilyl cation applied to TNT and RDX (153).

We turn now to investigations that included a report of detection sensitivity. In 1994, the CONDOR corona discharge APCI tandem quadrupole MS/MS system underwent a calibration study (154) that yielded minimum detection limits of 0.59, 5.2, and 0.39 μg for RDX, PETN, and TNT, respectively. By comparison, this work also was among those mentioned above as quantifying the mass of explosive in fingerprints. In this case, over 10 μg of RDX can be sampled from a thumbprint, even after 50 preceding prints following contact with solid explosive.

The calibration technique used for the CONDOR system involved direct liquid injection into the ionization region through a heated nebulizer. Similar techniques were used in two other recent studies. In their 1996 study of electron capture (EC) ionization of explosives, Cappiello et al (155) used a microflow rate particle beam interface and reported a detection limit for TNT of 120 μg at $S/N = 5$. They used a quadrupole mass spectrometer and observed that EC ionization with methane allows observation of a parent ion peak. Zhao et al (156) studied liquid sample injection into an atmospheric-pressure direct-current glow-discharge ionization source, reporting a TNT detection limit for their quadrupole mass spectrometer of 5.0 μg with $S/N = 3$. They also noted that this corresponded to a TNT concentration in the He carrier gas of 0.3 ppt_v, with total He flows through the instrument in the 1400–1600 STP $\text{cm}^3 \text{s}^{-1}$ range. In an earlier investigation by this group (157), LDI of TNT was quantified by drying measured amounts of solutions onto the desorption probe. The detection limit was reported as 280 μg , using the same quadrupole mass spectrometer and a nickel foil beta source instead of the glow discharge, but the system (which included an ion mobility spectrometer front end to the mass spectrometer) was said to be far from optimized. A more recent matrix-assisted

laser desorption ionization (MALDI) study (158) produced mass spectra (using a miniature TOF mass spectrometer, or “Tiny-TOF”) from less than 100 pg of RDX vaporized in a single laser pulse. However, the matrix chosen in this study had problems with adducts and molecular rearrangement.

In 1992, Glish and coworkers (159) presented signal-to-background ratios for detection of TNT, PETN, and RDX using three tandem mass spectrometric instruments: a quadrupole/TOF instrument, an ion trap mass spectrometer (ITMS), and a tandem quadrupole instrument. All instruments were interfaced to the same atmospheric sampling glow discharge ion source. Similar ratios were reported for all three instruments, in the range of 20 to 200 for about 1 ppb_v TNT and a 2-s data collection time. The ITMS was said to be the best of the three at that time and was subsequently shown (160) to have the capability of monitoring multiple compounds in parallel (in the published example, DNT, TNT, and tetryl). From the flow rates typical of the ionization source, we can deduce that an S/N = 2 concentration level of 10 ppt_v TNT for 2 s would correspond to roughly 0.01 pg TNT delivered into the instrument. Accounting for sampling losses, sensitivity determinations such as this are the basis for the statement (161) that with mass spectrometric instruments “sub-pg detection limits can be achieved, in favorable cases.” Using a TOF mass spectrometer and glow discharge atmospheric pressure ionization source, Lee et al (162) also reported a 0.01 pg TNT detection limit with S/N = 3, remarking that a 0.1-fg detection limit could be reached with minor modifications.

Ion Mobility Spectrometry

An ion mobility spectrometer is in some sense a TOF mass spectrometer that operates at atmospheric pressure. A sample, typically gaseous or in solution, is admitted into an ionization region, and gated packets of ions are accelerated by an electric field down a drift region against a flow of drift gas. This results in separation according to ion mobility, which depends on mass, charge, size, and shape. Detection is accomplished by measuring ion current from a Faraday plate. Ion mobility spectrometers have advantages of simplicity, small size, and short response time.

In contrast to mass spectroscopy at low pressures, where devices of several widely differing designs still deliver similar sensitivities, the literature on IMS reviewed here contains a broad range of reported detection limits. This may be due in part to sensitivity and selectivity tradeoffs. Broadly speaking, an ion mobility spectrometer by itself can operate with the sensitivity of a mass spectrometer, but with less selectivity. Therefore, sensitivities determined in the absence of interferences may be quite different than estimates made under more real-world conditions. In a recent overview of IMS for field screening

applications, Hill & Simpson (163) said "It is still difficult to find good quantitative data with respect to ion mobility spectrometry."

Estimates in the literature for the limits of detection of several commercially available devices do indeed vary by more than an order of magnitude. For example, the Barringer IONSCAN series of instruments (36, 164, 165) has been evaluated by Fetterolf and coworkers (166–169) to have 200-pg limits of detection for several of the common explosives. Hallowell et al (170) reported an RDX detection limit of approximately 20 pg using a PCP Model 110, and Davies et al (50) reported calibration studies using the same device that, for instance, yielded 95% confidence limits on an observation of 5 pg RDX of ± 14 pg. McGann et al (171, 172), describing the application of the IonTrack Ion Trap Mobility Spectrometer to narcotics and explosives, mention only a 115-pg detection limit for cocaine.

Efforts to improve IMS selectivity and sensitivity can focus either on the input to the device or on post-processing of the data. An investigation of the latter area by Lawrence et al (173) found that although the best sensitivity was obtained by spectrum analysis based on cross-correlation (leading to an RDX detection limit of 10 pg), this came at the expense of reduced selectivity, and a combination of cross-correlation to identify peaks and derivative techniques for final quantification should provide both sensitivity and selectivity. Among the options for improvement of selectivity at the input end are modifications of ion chemistry (see 174 for examples of the ions formed for various explosives and IMS parameters), and coupling to another separation device such as a gas chromatograph (42, 175). Simpson et al (175) reported GC/IMS detection limits for selected Environmental Protection Agency (EPA) priority pollutants, including a value for TNT of 0.71 pg/s. For a reasonable pulse width for the injected vapor, this corresponds to a minimum detectable mass of TNT of 5 pg, and for a typical carrier gas flow rate (10 ml/min), correlates with a vapor mixing ratio of about 0.5 ppb_v.

A particularly encouraging development in the IMS area is field ion spectrometry, also known as transverse field compensation ion mobility spectrometry (176). The basic difference is the application of two oscillating electric fields in the drift region. Sweeping the second, or compensating, field through a voltage range produces a spectrum. This technique eliminates the gating electrodes needed to pulse ions in conventional IMS, so ions are injected continuously, resulting in improved sensitivity.

Gas Chromatography

In the case of gas chromatography as applied to the separation and detection of explosives vapor, a third parameter is added to the critical ones of sensitivity

and selectivity: the time required for analysis. Substantial advances in speed have been achieved, but even though a recently developed commercial device using multicapillary columns [the Scintrex EVD-8000 (38, 177)] is reported to achieve detections in less than 60 s (177), this still precludes its applicability to a wide variety of screening roles. Using electron capture detection, this device's sensitivity limits are reported to be less than 1 ng for TNT and 5 ng for RDX (177). Ertl et al (178) also investigated multitube columns, achieving separation of a mixture of explosives in less than 2 min, while Holland et al (179) studied the use of two correlated microcolumns to reject interferences. Other recent investigations that could support further development are a tabulation of retention indices for a variety of explosives (180), a study of chromatographic techniques for laboratory analysis, including consideration of the optimum column temperature (181), and studies of the use of neural networks in data analysis (182, 183). Finally, we note again the potential for short-column gas chromatography to serve as a separation stage for an ion mobility spectrometer (42), leading to a device with excellent selectivity formed from two fast, sensitive devices with inadequate selectivity.

OTHER DETECTION METHODS

Immunosensors

Several approaches based on antigen-antibody formation have been investigated (184–189) besides the more physically based approaches described above. In these systems, a monoclonal antibody is developed by sensitizing test animals to a protein incorporating the substance to be detected or a close analog. When the substance to be detected binds to the antibody, a change in a property such as optical transmittance (184) or fluorescence (188) may be detected, registering the presence of the explosive. In continuous-flow immunosensors (185–187, 189) a flow of solution containing the analyte is exchanged with the immobilized antibody. Plastic beads containing the antibodies have been previously treated with a fluorescent dye-labeled explosive analog that is released to the solution when the explosive interacts with the antibody. The displaced analog molecules are then detected downstream by fluorescence excitation/emission spectroscopy.

Although such immunosensors are capable of sub parts-per-million detection of TNT, RDX, PETN, and related substances, their principal drawback for an application such as airport security screening is the time required to complete the analysis. For this reason, this technique has found its greatest use in analysis of explosive residues in soils and groundwater, rather than for real-time detection.

Synthetic Receptors: Molecular Recognition

One approach to high-selectivity detection of explosives at ultratrace levels that may overcome the processing time limitation of immunosensors is to combine a chemical sensor tailored to specific target molecules with a “molecular transducer” that responds nearly instantaneously to the presence of the analyte (190–197). The chemosensors consist of a molecular recognition site tailored to the target molecule, such as a polyrotaxane, cyclophane, or calixarene. The molecular transduction site may be based on fluorescence quenching, photoconductivity, or possibly surface-enhanced Raman scattering. Receptors for nitro-containing compounds have seen scant investigation to date, however, and much more work needs to be done in this area.

Olfaction

At the present time, there does exist a reasonably reliable, cost-effective, user-friendly biological system for explosives detection, namely, a trained dog and its handler (4, 198, 199). Explosive-sniffing dogs are still a key backup system at many airports and crime scenes. In 1994, the Federal Aviation Administration maintained 103 explosive detection dog handling teams for airport searches (170), and this number is expected to triple over the next several years. The Bureau of Alcohol, Tobacco, and Firearms maintains a dog-handler team that has participated in numerous searches during the past several years (200). Other species such as field mice (201) and gerbils (202) have been suggested for this purpose, but dogs remain the “system of choice” for this application.

Unlike mechanical instrumentation, however, trained dogs may be subject to boredom, distraction, unfamiliar signals, and/or inattention from handlers, as suggested by Figure 1. The process whereby dogs recognize and respond to odors is still not very well understood, and current research in this area is attempting to quantify such responses and improve the reliability of this already remarkable detection system. While it may eventually be possible to combine chemical sensors, readout devices, and neural network processing schemes to create an “electro-optic dog” that will reduce or eliminate the variability of the natural system, we have a long way to go before this can be accomplished.

CONCLUDING OBSERVATIONS

In this review, we have seen that detecting concealed explosives—and most importantly, preventing the tragic consequences of their unauthorized detonation—presents many challenges to the scientific community. In addition to developing sensitive and specific detectors, which has received the most attention to date, there is a great deal of information needed on the basic physical



"Yeah, but it doesn't smell like a bomb!"

Figure 1 Drawing by Cotham; © 1997, The New Yorker Magazine, Inc.

and chemical properties of these materials, including (a) vapor pressures, not only of pure materials but in compositions that may behave as highly nonideal solutions, (b) diffusivity and diffusion coefficients, (c) sticking coefficients on a wide range of surfaces, and (d) decomposition and fragmentation kinetics. This information is needed not only for the "classic" high explosive materials TNT, RDX, and PETN, but for the continually increasing variety of explosive compounds encountered by police and security agencies worldwide.

A specific instrumental approach that may be useful for overcoming the low sensitivity of standard optical techniques is cavity ringdown spectroscopy (CRDS) (203–207). In CRDS, the sample is introduced into a highly reflective resonant optical cavity, and the gradual decay of a laser pulse introduced into the cavity is used to detect weak absorptions. This technique has been capable of detecting single-pass absorptions in the range of 10^{-8} to 10^{-10} per cm and may be useful for detecting broad featureless absorption spectra such as those of explosive molecules at elevated temperatures, thereby affording the possibility of overcoming limited sample size with a relatively straightforward measurement technique.

The challenges in this field are not only technical ones. In science and engineering, the paradigm to which we are accustomed lies in meeting the challenges imposed by nature, as epitomized by Einstein:

The Good Lord is subtle, but He is not malicious (*Raffiniert is der Herrgott aber boshaft ist er nicht*). When asked by a colleague what he meant by that, [Einstein] replied: “Nature hides her secret because of her essential loftiness, but not by means of ruse” (208).

In the case of detecting concealed explosives, we are dealing with malicious aspects of human nature, sometimes called the “Dark Side” (209), among which may be included terrorist acts, drug abuse, and environmental degradation. These actions make use of the results of science (or technology), but turn them to purposes regarded as harmful by the great majority of people. Most perpetrators actively seek to conceal their actions to escape the sanctions imposed by society. The challenge is to use the insights provided by science and the tools provided by technology to thwart such destructive activities and to allow the underlying psychological, social, and economic motivations for these actions to be addressed in a rational, constructive, and compassionate way.

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